Effect of Starch on Tissue Waste/High Density Polyethylene/Starch Biocomposite for Thermoforming Process

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Abstract

Tissue waste is a problem for the tissue paper industry because the drying process and transporting of this waste are expensive. As a result this waste landed in land fill. Addition of starch in tissue waste suggests a good way to overcome the problem. Three different types of starch were used, corn starch, rice starch, and tapioca starch. However, starch blended with tissue waste produces products with weaknesses in strength, water resistance and cannot be thermoformed. HDPE as binder was added to improve these properties and processability. Melt flow index (MFI) is used to determine the processability and differential scanning calorimetry (DSC) to determine thermal behavior of the most suitable starch to the purpose of thermoforming process. Compounding was done on two-roll mill to form sheet prior to the thermoforming process. Results showed corn starch was most suitable starch base on tensile and water absorption test. Apart of that, by using DSC, corn starch demonstrated better compatibility between components in blends as it showed one melting point. Unfortunately, this formulation has low values of MFI due to high viscosity. Generally, this biocomposite formulation has similar characteristics to the molded casing made using synthetic polymer.

Keywords: Tissue waste; High density polyethylene; Starch; Thermoforming process; Biocomposite

1.0 INTRODUCTION

Nowadays, waste tissue paper is a problem for the tissue paper industry because the drying process and transporting of this waste are expensive. This is because tissue waste has high percentage of water content [1]. Because of this problem, many companies deposit this waste on neighboring land. The improper disposal of the material represents an environmental problem. Furthermore paper waste contain high content of cellulose fiber [2], can be used for other commercial and industrial applications.

The uses of cellulose fiber in packaging material have attracted many researchers to conduct the study and apply it on industry. This is because the cellulose fibers are well known as biodegradable material and friendly with nature. Thus, currently most study is based on blending non-biodegradable material such as plastic with biodegradable material like natural fibre and starch in order to achieve biodegradable material [3]. The reason fibrous starch and natural fibre are chosen not only due to its environmental friendly but also have good mechanical properties, such as impact resistance at very low weight.[4]

The using of starch and fiber have made the blend more degradable to nature but it have same problem with natural fiber which hydrophilic in nature.[5] Therefore in this study, combination of starch and plastic (HDPE) were used as binder in blending tissue paper in order to improve thermoform compatibility and water resistance properties.

2.0 MATERIALS AND METHODS

2.1 Materials

The core material used in this study is waste tissue paper which acts as the matrix. While the other materials such as high density polyethylene (HDPE) and starch was used as a binder. The main properties of the waste tissue paper include absorbency, wet tensile strength, and softness [6]. A solid waste rich in non-extracted tissue paper obtained from the industrial production of tissue paper was used to

obtain a composite that is similar to bagasse [7-8]. The types of materials used in the waste tissue paper formulations are shown in Table 1.

Table 1: Types of Materials

Materials	Types
Base Material	Waste Tissue Paper
Binder	High Density Polyethylene (HDPE)
Fibrous starch	Corn Starch
	Tapioca Starch
	Rice Starch

High density polyethylene (HDPE) TITANZEX HB6200 with a specified melt flow index of 0.45 g/10 minutes was supplied by Titan Petchem (M) Sdn. Bhd. The properties of TITANZEX HB6200 are summarized in Table 2. This resin was originally in the form of extruded pellets.

Table 2: The Properties of HDPE

Properties	TITANZEX HB6200
Density (g/cm^3)	0.956
Melt Index (g/10 min)	0.45 (at 190°C)
Vicat Softening Point (°C)	128
Tensile strength at yield (kg/cm^2)	270
Elongation at break (%)	>500

2.2 Methods

2.2.1 Blend Preparation

Waste tissue paper was dried in order to remove water from the sample. Water content in the waste tissue paper was 69.65%. Percentage of water content can be calculated according to ASTM D570-98 by using the equation 1:

$$\% Mt = \frac{Ww - Wd}{Wd} \times 100\% \quad (1)$$

Where; Ww = Wet weight;

Wd = Dry weight;

%Mt = Percentage of Water

After the tissue waste was dried, the dry blending was applied to ensure all the incorporated binder and fibres were well dispersed and distributed in the waste tissue paper. These composites were continuously compounded for 5 minutes on two roll mill and sheeted at 145 °C for 10-15 minutes. The waste tissue paper dry blend formulations showed in Table 3.

Table 3: Blend Formulation of Waste Tissue Paper

Sample	Type of Starch	Ingredients (%)		
		Waste Tissue Paper	HDPE	Starch
1	Corn	32	20	48
2	Tapioca	32	20	48
3	Rice	32	20	48

2.2.2 Properties Determination

2.2.2.1 Tensile Test

The tensile properties were determined by using tensile testing machine (Lloyd Machine), according to the ASTM D638 standard. The load cell capacity of 100N was used at a rate of 1 mm/min. The samples from the same group were used in order to determine average values of tensile strength, elongation at break and Young's modulus [9].

2.2.2.2 Water Absorption Test

For water absorption experiments, five samples from the same group were used to establish the average values of water absorption for each group. Samples of each material were cut into 1mm x 1mm dimension and dried in vacuum oven for 24 hours at 50+/-5 °C, and immediately weighed to the nearest 0.0001g. The conditioned specimens were rested on their edge and completely immersed in a container of distilled water (ASTM D570). After three days, the specimens were removed from the water one at a time, wiped with a dry cloth to remove all surface water, and weighed to the nearest 0.0001g. The samples were then returned to the distilled water. Thereafter, the samples were weighed every three days for three weeks [10].

2.2.3 Thermoforming Process Parameters Optimization

In this study, drape-forming was used. Drape-forming is one of the common prestretching methods which compressed air is used to inflate the sheet into a bubble [11]. The force is limited to that available from atmospheric pressure, usually 10-12 psi [12].

2.2.4 Thermal Analysis

Thermal analysis was done using a model Differential Scanning Calorimeter (DSC) 7 Perkin Elmer under a nitrogen atmosphere. The method is applied in a conventional heat flux calorimeter, to obtain thermal analysis data having improved baseline and resolution [13].

Samples weighing between 10-12 mg were placed into aluminum pan were compressed and sealed was. Analysis was carried out at a heating rate of 10°C/min and at temperature ranging from 30°C to 250°C. The tangent method was used to determine the melting temperature (T_m) of the samples. The mid-point of the first endothermic baseline shift in the DSC heating curve was taken as the T_m.

2.2.5 Melt Flow Index (MFI)

MFI measurements of tissue waste, high density polyethylene and starch blends were obtained by using extrusion plastometer, according to ASTM D1238 (procedure A, 220 °C/10kg and 230 °C/10kg).

3.0 RESULTS AND DISCUSSION

3.1 Properties Determination

3.1 Tensile Test

Table 4 shows the average maximum tensile strength, Young's Modulus, and maximum elongation at break for tissue waste/HDPE/starch biocomposite with different starch.

Table 4: Average values for maximum tensile strength, Young's Modulus, and maximum elongation at break for tissue waste/HDPE/starch compound.

Materials	Average tensile strength (MPa)	Average Young's Modulus (MPa)	Average elongation at break (%)
Tissue Waste / HDPE / Corn Starch	8.99	736.50	7.49
Tissue Waste / HDPE / Rice Starch	4.53	520.05	2.68
Tissue Waste / HDPE / Tapioca Starch	3.53	475.85	1.10

Formulation of tissue waste and high density polyethylene (HDPE) with corn starch gave high values of maximum tensile strength, Young's Modulus, and maximum elongation at break. These are due to corn starch contains the highest

amylose content compared to tapioca starch and rice starch. An increased in the tensile strength value of tissue waste/HDPE/starch blends occurred when there is a slight increase in amylose content in the blends, thus tensile properties of tissue waste/HDPE/starch were dependent on amylose/amylopectin ratio. Besides, in this blends, the increase in tensile strength with amylose content is due to the higher viscosities of high amylose corn starches. During processing the higher viscosities led to the higher stresses and caused the starch granules to melt and form a co-continuous phase with synthetic polymer which increased the tensile strength in the blends [14].

Highest tensile strength of tissue waste/HDPE/corn starch blends observed is also because of the strongest interfacial adhesion between corn starch and tissue waste/HDPE blends. The increment in tensile strength of HDPE/starch blends could be due to the increment in interfacial adhesion resulting from the reaction between HDPE and starch as reported by previous researcher[15]. Formulation of tissue waste/HDPE with rice starch and tapioca starch showed lower tensile strength. A possible explanation for the decrement in tensile strength after addition of starch to HDPE could be the low interfacial interaction between the components of the blend, that lead to mechanical rupture at the blend interface [16]. The weakness of interfacial adhesion may probably occur because of the hydrophilic nature of rice and tapioca starch which are not compatible with hydrophobic HDPE polymers [10].

Similar to tensile strength, increasing or decreasing of elongation at break arise because of the influence of interfacial adhesion between starch and HDPE. Wan Aizan *et al*, reported that, the addition of fibrous sago waste to a ductile matrix HDPE has decreased the elongation properties at break [10]. Furthermore, Nikazar *et al*, states that the incorporation of corn starch granules in the LDPE matrix has a negative influence on the stretching properties of the plastic [17]. Results showed that the addition of all type of starches to HDPE gave insufficient elongation at break, however corn starch gave the highest result. The elongation therefore depends on the state of the interfacial interaction between the phases of the blend [16].

Corn starch in tissue waste/HDPE showed highest Young's modulus indicating blends with corn starch is much stiffer. This is because during processing, the starch granules did not melt and retained their granules shape. These granules are stiff and act as rigid fillers. Since the Young's Modulus is closely related to the rigid domains of the material therefore the value of Young's Modulus is dependent on the

rigidity associated with starch agglomerates [16]. Moreover, the modulus increased due to the stiffening effect of the starch granules, as the starch is stiffer than PE. Since the starch contains both amorphous and crystalline region, the calculated starch moduli are averages which reflect the contribution of each phase. Thus, corn starch was stiffer and more rigid compared to rice starch and tapioca starch [15].

Basically, there is also an interaction between the effect of starch's type and concentration on the tensile properties of starch and polyethylene blends. According to Mani *et al*, high tensile strength observed presumably due to the crosslinking between highly branched amylopectin of the starch and the synthetic polymers [14]. The value of tensile properties also depends on cross-sectional area of starch. The drop in tensile strength is in accordance with the decrease in the effective cross-sectional area for spherical particulate fillers [18-19].

3.1.2 Water Absorption Test

As one of the major drawbacks in the use of starch based materials is their water absorption tendency, any improvement in water resistance is highly important [20]. The key justification of this drawback is the hydroxyl group in starch can form a hydrogen bond with water [14]. Water molecules may act as a natural plasticizer for starch, which helps render starch flexibility as compared to hard and rigid filler in its completely dry state [18]. Influence of the starch type on water absorption of these blends as a function of time is shown in Figure 1.

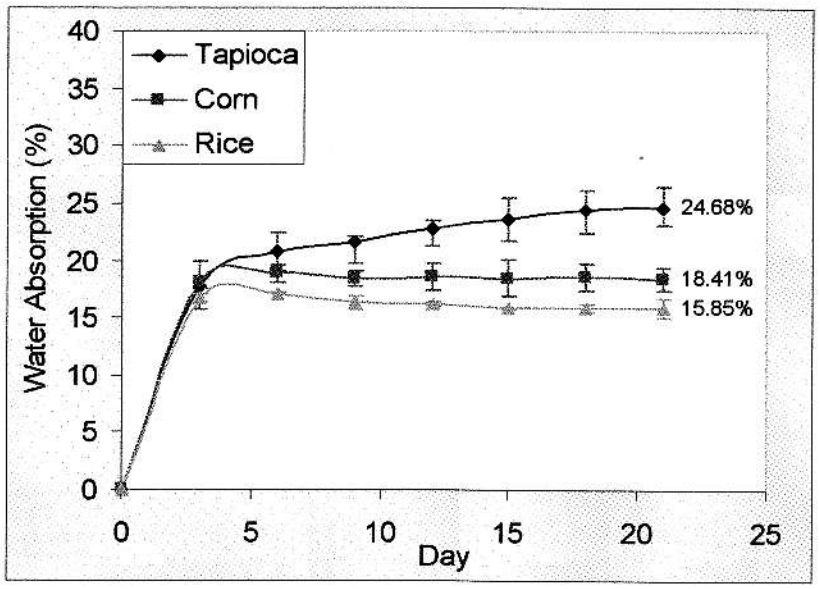

Figure 1: Percentages of water absorption for tissue waste/HDPE/starch composites with time of immersion.

Rate of water absorption was high in the first 4 days, after which a steady state is reached indicative of saturation. A rapid moisture uptake is observed within a few days of immersion, but this decreased slowly with time. The decreased in the rate of moisture uptake with time of immersion could be due to a concentration gradient across the materials. Initially water molecules added to starch particles is strongly bonded as in a hydrate. Whereby, water penetrated into the films and bonded to the hydroxyl group of starch granules swelled and reduced the gap between their molecules and space to the matrix molecules. Water is difficult to diffuse thus rate of water uptake is reduced [10]. Besides, the water molecules could saturate the surface of the synthetic polymer/starch composites easily and also penetrate into the composites through voids, resulting in higher water absorption in a short exposure time. Water absorption may drop slightly as immersion time is increased, owing to the fact that some starch particle was leached away from the specimen [18]. A potential drawback in the starch blend is the possibility of material leaching into the liquid. It was suggested that upon water uptake, the starch granules swelled up, increased in size and being forced out [14]. HDPE does not swell proportionately with starch, because it is a poor water absorber.

From Figure 1, tapioca starch samples show the highest percentage of water absorption compared with samples of corn starch and rice starch which show lower

water absorption rates. The feasible explanation is water absorption decreases as the amylose content increases in the starch blends. Tapioca starch has lower amylose content than corn starch [19]. Therefore, tapioca starch show higher water uptake compared to corn starch. In all cases, both the equilibrium water uptake and rate of water uptake are lower in the blends containing high amylose contents of 70% and higher in the case of starch blends. This is probably due to increased gelatinization and degradation of the branched structure of amylopectin in the starch blends that make the blend more water sensitive [14]. Furthermore, the action of water may have resulted in a further disruption of the interfacial adhesion between the starch granules and synthetic polymer matrix. Subsequently, these will probably lead to the formation of additional voids in the synthetic polymer/starch composites, which would then be filled with water (water entrapment in the matrix). Upon drying, these voids will act as stress concentrators, which can then initiate matrix cracking, leading to reductions in both stiffness and strength of the composites. This is in agreement with the observed embrittlement of the composites and explains the dramatic drop of the elongation at break values [18].

In this study, although rice starch has same amylose content with tapioca starch, this starch totally gave different result from the theory. Rice starch samples show lowest percentage of water absorption. This behavior could be related to the lower processing temperature which could lead to lower degradation of starch and hence a decrease in the water absorption rate [14].

3.2 Thermoforming Process Parameters Approximation

3.2.1 Thermal Analysis

Mainly, the principle of this thermal analysis is to determine the melting temperature for certain materials, especially for new formulations. This is because there is no exact melting point for new formulations. By using DSC, the appropriate melting point can be obtained and the thermoforming process parameters can be predicted without doing the trial and error to identify the process temperature. Just below melt temperature, the materials will start to deform according to the mold shape. Figure 2 illustrates the thermograms for tissue waste/HDPE/starch blends. It showed one melting peak (at 128.63°C), indicating that the material demonstrate

greater compatibility between components in blends. However, the portion of the curve related to tissue waste/HDPE/corn starch blend, the ΔH values was low (at 40.63J/g), indicating that this blend had a low degree of crystallinity. The greater the compatibility between components in blends, the weaker will be their ability to crystallize [21].

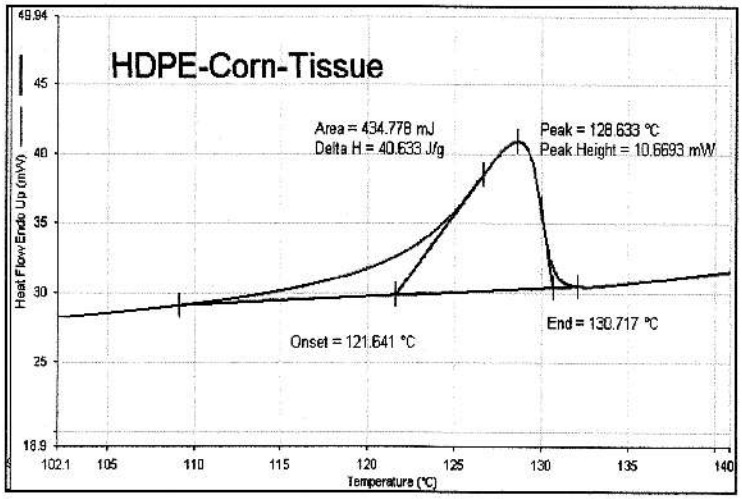

Figure 2: DSC curves for tissue waste/HDPE/corn starch blends

3.2.2 Melt Flow Index (MFI)

Fundamentally, the main objective of this MFI is to verify the extrusion rate of materials. In this study, high MFI values are needed since thermoforming process employ high load during process. The melt flow index (MFI) values for tissue waste/HDPE/corn starch blends are showed in Table 5. Since the MFI is an indirect measurement of material viscosity, these results indicated that tissue waste/HDPE/corn starch blends had a high viscosity. It was not possible to determine the MFI of the starch blends using a load of 2.16 kg since their viscosity were so high that an excessively long period would be needed before any measurements could be done [16].

Table 5: MFI value of Tissue Waste/HDPE/Corn Starch blends.

Temperature (°C)	**Load (kg)**	**Result (g/10min)**
220	10.00	0.3944
230	10.00	0.2884

The MFI values could be only obtained when using temperature of 220°C and 230°C at 10 kg load. The difficulty of this measurement was probably due to the starch itself. The starch act as rigid filler since the main effect of rigid fillers is to increase the elastic modulus of a composite or the viscosity of a fluid suspension [16].

The MFI values decreased as the temperature increase. From the observation, the blends start to degrade under high temperature at long period of time. Thus, when this blend starts to degrade, there was no flow observed. The degradation happened because the melting temperature of tissue waste/HDPE/corn starch is 128.63°C but the temperature used in the MFI was much higher. Moreover, this blend takes a long time to melt (flow) due to their high viscosity. Even though, under high temperature processing, starch granules can still retained their shape and functioned as rigid particulate fillers. The flows of matrix synthetic polymer are restricted by the starch particles and thus, increased the viscosity of the blend [10].

In addition, the large amount of starch will make the interaction among the granules stronger and contributes to the higher viscosity. For high loading starch, the spaces between particle-particle are small. If the particle-particle interactions are stronger than particle-matrix interaction, agglomeration of particles may occur and result in the immobilization of more matrix molecules. The matrix molecules become trapped in starch particles as the size of agglomerates rise and flows have been confined [10]. In this study, the optimum was at 48% loading of starch.

4.0 CONCLUSIONS

Formulation of tissue waste and high density polyethylene (HDPE) with corn starch show paramount values of maximum tensile strength, Young's Modulus and maximum elongation at break compared to formulation with rice starch and tapioca starch. Higher amylose content and strongest interfacial adhesion between corn starch and tissue waste/HDPE blends are probably the reasons. Young's modulus of tissue waste/HDPE/corn starch blend shows better result due to the stiffening effect of the starch granules. Melt flow index (MFI) values of the tissue waste/HDPE/corn starch are low due to high viscosity of the formulation. With respect to water absorption properties, each starch showed strong absorption due to the subsistence

hydroxyl group in starch that can form a hydrogen bond with water molecules. In this test, tapioca starch has highest percentage of water absorption.

Thermal analysis of tissue waste/HDPE/corn starch, demonstrate greater compatibility between components in blends compared to rice and topiaca starch corresponding to the tensile properties result.

ACKNOWLEDGEMENT

The authors would like to express their thanks to UTM, FRGS grant vot 78039 and Titan Petchem (M) Sdn. Bhd. for materials support throughout this work.

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